# A Combined Solvent Extraction and Tanning Process

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## ABSTRACT

Dehaired hides were tanned, without preliminary dehydration, with a suspension of solid tanning material in acetone. The wet hides provided enough water to effect solution of the tannin. This system eliminates two steps of other solvent tanning systems: the dehydration of the pelt and the preparation of a tannin solution in the solvent. The results of small-scale tanning tests are promising.

## INTRODUCTION

The use of organic solvents as an aid in the extraction of tannin and in the tanning of heavy leather has been suggested. Luvisi, Cordon, Beebe and Rogers (4) in 1949 proposed the extraction of tannin from canaigre by aqueous solutions of various alcohols, or preferably of acetone. Roddy (6) in 1943 published the results of tanning tests using acetone solutions of tanning material. Kremen in 1955 (3) demonstrated the possible advantages of such tannages.

As shown by Stather, Lauffmann and Bau Miau (7) in 1936, pure acetone is a poor solvent for tannin. Of all the common tanning materials, only quebracho is sufficiently soluble to be of use in a system such as proposed by Kremen. Wattle is moderately soluble. However, mixtures of acetone and water, in a wide range of concentrations, are very good solvents for tannins. The use of such mixtures greatly increases the speed of extraction and the amount of tannin extracted compared with either pure acetone or water.

The cost of an organic solvent either for tannin extraction or for tanning would be prohibitive unless the solvent were recovered. Even in this case, the cost of the recovery process would be considerable. If tannin were extracted by an organic solvent-and-water process, and the extract thus prepared were used for tanning by a solvent process, two recovery steps would be required. However, if the two processes could be combined, the advantages of both could be obtained with only one recovery step. We have devised such a process using acetone as a solvent. This process has a further advantage over other solvent processes in that it is not necessary to dehydrate the hides before tannage. Although applicable to any tanning material, it is particularly advantageous for materials of high tannin content, such as canaigre roots or wattle bark, which were used in these tests.

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## TANNING PROCEDURE

The hides, prepared as usual for tanning (by soaking, liming, unhairing, fleshing, and washing or bating slightly as desired), are put into a tanning drum. The calculated amount of finely ground tanning material is then added together with the required amount of acetone. The drum is turned intermittently at a slow rate for several hours. Penetration of tannin into the hide is slow at first because of the low solubility of tannin in acetone. However, as water diffuses from the hide, a solution of acetone and water is formed which is a better solvent for tannin. As the solution penetrates into the hide some combination takes place between the hide and the tannin because of the presence of water in the hide. Because the concentration of tannin in the solution is low at first and increases gradually, full penetration is obtained without any trace of case hardening. The time required for penetration is about 16 hours. This is somewhat longer than the time required for penetration in other solvent tannages but since dehydration of the hides is not required, the total time is approximately the same. In addition, the cost of the dehydration process is eliminated. The moderate amount of tannage taking place during the impregnation by the acetone solution is an advantage in that it puts the hide in better condition for subsequent processing.

After complete penetration of tannin from the acetone solution, the hides are drained and treated with a strong, aqueous tanning liquor prepared as described later. This corresponds to the usual "extracting" procedure in tanning. The speed of the drums should be considerably slower than the usual speed of "extract" drums to prevent damage to the hides before they are sufficiently tanned. The drums should be turned intermittently at first. The "extracting" step will thus require somewhat more time than the usual extracting procedure but still will not require more than three or four hours. After "extracting", the leather is finished by normal procedures. The time required from beamhouse to bleach vats should be three or four days.

The acetone is recovered from the solution by distillation. The remaining aqueous solution is filtered and, if desired, sulfited. This liquor is used for the extracting step. The process may be adjusted so that the amount of liquor prepared from the acetone solution is exactly that required for the "extracting" step, or so that addition of a slight amount of commercial extract will be required.

## EXPERIMENTAL

Some of the factors involved in this process are: the kind of tanning material used, the size of the grind, the duration of each step, and the manner of "extracting". The following experiments are indicative of the partial evaluation of some of these factors. The results are summarized in Table I.

In Experiments 1 to 6, both stages of the process were carried out in a Meissner mill, 24 inches in diameter, making eight turns a minute. This was run intermittently for five minutes of every half-hour. All hide pieces were cut from the bend portion of a hide which had been prepared in the usual manner for tanning.

TABLE I

SUMMARY OF EXPERIMENTS

| Experiment No. | Hide Wgt. | Tanning Material Source* | Tanning Material | Grind Mesh | Volume of Acetone | Amt. 40° Tw. Liquor for Extracting | Time in Acetone | Leather Yield† | Tannin in Spents |
|---|---|---|---|---|---|---|---|---|---|
| | g. | | g. | | l. | ml. | hr. | % | % |
| 1 | 227 | Canaigre | 300 | 20 | 1.3 | 140 | 24 | 71.8 | 7.4 |
| | 223 | | | | | | | 70.9 | |
| 2 | 249 | Canaigre | 166 | 9 | 0.44 | 74 | 8 | 56.0 | 12.3 |
| 3 | 217 | Canaigre | 145 | 20 | 0.39 | 66 | 8 | 67.0 | 5 9 |
| 4 | 282 | Canaigre | 189 | 20 | 0.75 | 85 | 24 | 76.9 | 5.8 |
| 5 | 318 | Wattle | 230 | 20 | 1.85 | 125 | 24 | 69.6 | 2.7 |
| 6 | 337 | Wattle | 300 | 20 | 1.86 | 165 | 24 | 70.7 | 3.2 |
| 7 | 4332 | Canaigre | 6,000 | 20 | 75.6 | 50,000 | 24 | 71.9‡ | 9.9 |
| | 4453 | | | | | | | 70 9 | |
| 8 | 4830 | Wattle | 4,540 | 20 | 75.6 | 50,000 | 24 | 72.8 | 13.5 |
| | 4850 | | | | | | | 73.0 | |

*Tannin in material as used—canaigre 33%; wattle 39%.

†Finished weight as percentage of white weight.

‡Yields of comparable bends tanned at a commercial tannery were 77.5 and 77.3%.

The spents were analyzed by the official methods of the American Leather Chemists Association (1) except that the method of Luvisi and Rogers (5) was used to prepare the analytical solution of the canaigre.

**Experiment 1.**—Two pieces were tanned as indicated in Table I. After impregnation with tannin in the acetone solution they were taken out and wrapped in cloth to prevent drying out. The total liquor, including the rinsings, was distilled to recover the acetone. The aqueous solution was settled by standing for four hours and the supernatant evaporated under vacuum to give a 40° Tw. liquor. This was treated with 5% sodium bisulfite based on the weight of solids. This liquor was swabbed and rubbed into the leather pieces to simulate the effect of "extracting". The pieces were sammied for two days, after which they were bleached, oiled and dried. The total operating time from beamhouse to oiling was three days. The leather was firm, of good color, well and uniformly filled with tannin and had no drawn grain or other visible defect. Considering the peculiar nature of canaigre, the analysis of the spents indicated that a satisfactory extraction of the tannin had been obtained.

**Experiments 2 and 3.**—These indicate the effect of fineness of grind of the tanning material and of time in the acetone solution on the pick-up of tannin. In Experiment 2 penetration of tannin into the hide was unsatisfactory, and leather yields were low. In Experiment 3 the use of finely ground material resulted in satisfactory tanning even in eight hours. A somewhat longer period might be advantageous, since exposure to the acetone solution for 24 hours resulted in a definitely higher yield.

**Experiment 4.**—In the preceding tests it was necessary to hold the leather pieces one day after taking them from the acetone solution, until the acetone had been distilled and the liquors concentrated. This would not be done in practice. Therefore, a test was made in which the leather, after being removed from the acetone, was treated immediately with an extract equivalent in quantity and composition to that which could have been produced from the acetone liquor. Leather of comparable quality and good yields was obtained.

**Experiments 5 and 6.**—These experiments were conducted in the same manner as in Experiment 1, except that wattle bark was used as the source of tannin. The leather produced was of good quality. The spents were analyzed by the official methods of the American Leather Chemists Association (1).

In all the preceding experiments the leather yields give an approximation of what might be expected in practice but since the pieces were cut from different portions of the same hide, variations in yield might be expected.

In Experiments 7 and 8 tannage was carried out on a larger scale, using bends. Because of restrictions upon the use of volatile solvents, the tannage could not be carried out in the most desirable manner, which would be in drums or in enclosed vats with vigorous stirring. For the tannage a vat 4½ inches wide, and long and deep enough for a bend was used. To keep the tanning material in suspension, a stirrer was placed at each end of the vat. Each stirrer had a vane near the bottom of the vat, and one about halfway to the top. These vanes were only two inches in diameter, however, and did not keep the powdered material in the state of suspension necessary for the most efficient extraction. No equipment was available for recovery of the solvent and preparation of the "extracting" liquor. Therefore, for this purpose a liquor was made from powdered extracts; for the canaigre tannage a sulfited canaigre extract was used and for the wattle tannage a sulfited quebracho extract. Since the size of the tanning drum was disproportionate to the size of the bends, it was necessary to use a larger "float" than usual. For these reasons, a satisfactory tannin balance cannot be calculated for these experiments. This does not affect the evaluation of the leather produced.

**Experiment 7.**—Two hides were obtained from a tannery cold pool. Two bends were cut from each hide, one of which was sent to the tannery to be

tanned and finished in the usual manner. The other was tanned by the solvent process at the laboratory. After immersing the bends in the acetone, the stirrers were run for six hours, the settled material on the bottom being occasionally mixed with a paddle. The bends remained in the liquor overnight without stirring. The following morning the stirrers were run for two hours. The leather was removed, drained for ½ hour, and placed in a tanning drum containing sulfited canaigre extract of 40° Tw. The drum was turned intermittently for six hours—five minutes turning and 25 minutes standing. The bends were left in the drum overnight without turning. The drum was then turned slowly and steadily for two hours. The bends were taken out, sammied for two days, and returned to the tannery for bleaching, oiling, and finishing. They were saved for comparison with the bends finished by the regular process. The total time between white pool and bleach was seven days; the actual operating time was five days. The leather produced was uniformly tanned throughout the whole cross section; there was no drawn grain or other defect, and the color was exceptionally good. A slightly "empty" feel to the leather was confirmed by the yields, which were somewhat low for the laboratory as compared to the tannery bends. The rather low yields of the leather and high tannin content of the spents were probably due to the somewhat unsatisfactory method of operation. The analysis of the leather obtained is shown in Table II.

TABLE II

ANALYSES OF FINISHED BENDS

CALCULATED ON MOISTURE-FREE BASIS

| | Experiment 7 | | Experiment 8 |
|---|---|---|---|
| | *Solvent-Tanned with Canaigre* | *Commercially Tanned** | *Solvent-Tanned with Wattle* |
| Petroleum ether extract (%) | 5.4 | 6.0 | 4.8 |
| Insoluble ash (%) | 0.2 | 0.2 | 0.3 |
| Hide substance (%) | 43.4 | 34.4 | 40.4 |
| Soluble matter (%) | 29.3 | 37.9 | 31.5 |
| Combined tannin (%) | 21.7 | 21.5 | 23.0 |
| Total (%) | 100.0 | 100.0 | 100.0 |
| Degree of tannage (%) | 50.1 | 62.7 | 56.9 |
| Soluble nontannin (%) | 19.8 | 27.8 | 19.0 |
| Soluble tannin (%) | 9.5 | 10.1 | 10.3 |
| pH † | 4.3 | 3.8 | 4.4 |

*Comparable bends tanned with usual tanning blend at a commercial tannery.

†Determined on air-dry leather according to official methods of the American Leather Chemists Association.(2).

**Experiment 8.**—This tannage was conducted in a manner similar to Experiment 7, except that wattle was used in place of canaigre. An excess was

used in order to produce a well filled piece of leather, although it was felt that this would increase the tannin remaining in the spents. No tannery comparisons were made of this tannage. Both bends of the hide were used for the solvent tannage. The tanning operation was the same as in Experiment 7, except that sulfited quebracho was used for the second stage. The yields were somewhat better than in Experiment 7, but, as expected, the tannin remaining in the spents was high. The leather was of good quality and did not have the "empty" feel of the canaigre bends. Analysis of the leather is shown in Table II. The experiment might have been more realistic had it been possible to use an extract for the second stage prepared from the acetone liquor of the first stage. However, tests have indicated that the use of an equivalent solution does not influence the results to an appreciable extent.

## DISCUSSION

The advantages of solvent tannage, as outlined by Kremen, would also apply to this tannage: the rocker and layaway yards are eliminated and the time required for the tanning process is reduced. The inventory and labor needed are consequently reduced, although the advantage is at least counterbalanced by the necessity for a solvent-recovery process. The shorter time of tannage also allows a more rapid response to changing conditions such as fluctuations in hide prices or demands for different types of leather. Other advantages are reduction of sewage-disposal problems and possible use of the solvent to introduce desirable materials into the leather. The disadvantages in the use of a volatile solvent are, in addition to the requirements of a recovery system, the loss of solvent, the necessity of adopting safety measures against fire, and the fact that existing tannery equipment cannot be used without modification.

The advantages of the method described here are that it combines tanning and extraction into one operation, and uses a more efficient means of extracting the tannin from the raw material. Furthermore, it does not require dehydration of the hides before tanning.

The method would also be applicable to other tanning materials, but for operational and economic reasons it is probably most suited to those of high tannin content, such as canaigre roots or wattle bark. It is possible that the advantages of using hides which have not been dehydrated might be extended to the use of tanning extracts instead of raw tanning materials as suggested by Roddy (6). In this case the extract would be added to acetone at intervals in gradually increasing portions.

The leather yields and the analyses indicate that the leathers were not as thoroughly tanned as normal leather. However, the conditions used were not optimum. It seems quite possible that by improving the conditions of tanning and modifying the finishing processes, yields of leather comparable to those of usual tanning operations may be obtained.

## REFERENCES


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